OFFICE OF NAVAL RESEARCH

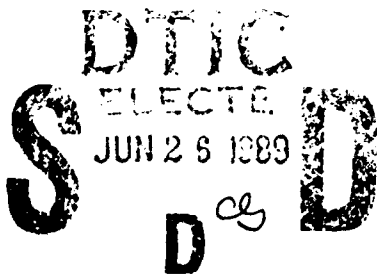## The Use of Multiple Ion Exchange to Produce Energy Transfer in Beta" Aluminas

by

L.A. Momoda, J.D. Barrie and B. Dunn

Prepared for Publication

in

Materials Research Bulletin

Department of Materials Science and Engineering
University of California, Los Angeles,
Los Angeles, California   90024

June 15, 1989

89   6 26 033

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
	Approved for Public use and sale; its distribution is unlimited
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Technical Report No. 19	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Department of Materials Science and Engineering		Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
6531 Boelter Hall University of California, Los Angeles Los Angeles, CA 90024-1595	Chemistry Division 800 N. Quincy Street Arlington, VA 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Office of Naval Research		N00014-83-K-0498

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
Chemistry Division 800 N. Quincy Street Arlington, VA 22217	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
Use of Multiple Ion Exchange to Produce Energy Transfer in β''-Aluminas

12. PERSONAL AUTHOR(S)
L. A. Momoda, J. D. Barrie, B. Dunn

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM 8/88 TO 7/89	1989, June 15	8

16. SUPPLEMENTARY NOTATION
Submitted to Materials Research Bulletin

17	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	energy transfer, beta" alumina, up-conversion, ion exchange

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The preparation of single crystals of β"-alumina containing two trivalent lanthanide species is described. The use of eutectic melts enables the two rare earth species to be introduced during a single ion exchange process. Energy transfer in crystals containing Ce^{+3}/Nd^{+3} and Ce^{+3}/Tb^{+3} is shown. High transfer efficiencies were measured for crystals with low sensitizer-to-activator ion concentration ratios. Up-conversion processes were observed in crystals doped with Yb^{+3} and Er^{+3} ions.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION	
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Bruce Dunn	(213) 825-1519	

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.   SECURITY CLASSIFICATION OF THIS PAGE

THE USE OF MULTIPLE ION EXCHANGE TO PRODUCE ENERGY TRANSFER IN BETA"-ALUMINAS

L.A. Momoda, J.D. Barrie and B. Dunn
Department of Materials Science and Engineering
University of California, Los Angeles 90024

ABSTRACT

The preparation of single crystals of ß"-alumina containing two trivalent lanthanide species is described. The use of eutectic melts enables the two rare earth species to be introduced during a single ion exchange process. Energy transfer in crystals containing Ce^{+3}/Nd^{+3} and Ce^{+3}/Tb^{+3} is shown. High transfer efficiencies were measured for crystals with low sensitizer-to-activator ion concentration ratios. Up-conversion processes were observed in crystals doped with Yb^{+3} and Er^{+3} ions.

MATERIALS INDEX: ß"-alumina, ion exchange, energy transfer.

Introduction

Sodium-ß"-alumina (nominally $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$) is a well-known solid electrolyte which has the unique ability to readily exchange the sodium ions in its structure for a wide variety of mono-, di- and trivalent ionic species (1,2). The ß"-alumina isomorphs produced by this technique exhibit a variety of interesting transport and optical properties. The ion exchange process is particularly useful for optical materials because it allows the separation of the doping process from that of crystal growth. In this way there is an opportunity to effectively control the valence and the concentration of the dopant ion in the ß"-alumina host.

The optical properties of many of the ß"-alumina crystals individually exchanged with lanthanide and transition metal ions have been investigated (3-6). The ion exchange of a second optical ion into the material (double doping) is also of considerable interest because of the prospects for energy transfer. Energy transfer has long been used as a means of increasing the absorption cross section of materials containing the weakly absorbing trivalent lanthanide ions (7). The electronic coupling of lanthanide ions (activating ions) to other more strongly absorbing ions (sensitizing ions), such as Ce^{+3} which has a highly allowed $4f \rightarrow 5d$ transition, is of practical importance for increasing the pumping efficiencies of solid state laser and phosphor materials.

The present paper considers the preparation and properties of ß"-aluminas which have been simultaneously exchanged with both sensitizers and activators. The double ion exchange process is found to be effective for different lanthanide couples (Ce^{+3}/Nd^{+3}, Ce^{+3}/Tb^{+3}, Yb^{+3}/Er^{+3}) and the sensitizer/activator ratio can be varied over a wide range. The ions are homogeneously

distributed within the material and energy transfer effects are observed.

Experimental Methods

1) Synthesis

The exchange of Na^+ ions in Na^+-ß"-alumina for two optically active species was achieved by modifying a method used for trivalent lanthanide exchanges (2). Each sensitizing and activating specie was introduced as the corresponding hydrated chloride salt (REacton, 99.99%). Eutectic mixtures of each lanthanide chloride with NaCl were individually mixed and ground. The amount of each eutectic mixture added to the batch determined the relative concentrations of sensitizer and activator in the melt and, ultimately, in the crystal. In each experiment, there was a large excess of melt so that the melt composition was essentially unaffected by the ion exchange process.

Before each exchange, the salt mixture was pre-dried to prevent the decomposition of the hydrated lanthanide chloride to the oxychloride. Oxychlorides are very refractory and inhibit the formation of the low temperature melts necessary for ion exchange. The Ce^{+3}/Nd^{+3} and Ce^{+3}/Tb^{+3} salt mixtures were pre-treated by slow drying under vacuum atmospheres. The $ErCl_3$ and $YbCl_3$ salts, however, decomposed more readily and the slow vacuum pre-drying was not sufficient to prevent oxychloride formation. For these salts, a dehydration method involving slow drying under chlorine atmospheres in the presence of excess ammonium chloride was used (8).

The dried salts were placed in a quartz retort, heated slowly to 650°C under chlorine atmosphere and held at this temperature until the salts were molten. The Na^+-ß"-alumina crystals (3mm x 3mm x 0.3 mm thick) were then immersed in the molten salt for 1 hour. After the crystals were removed from the melt, the entire assembly was cooled to room temperature over a period of approximately 2 hours. In all cases, the optical quality of the exchanged crystals was not degraded by exposure to the molten salts.

The composition of the exchanged crystals was characterized in two steps. First, the total concentration of optically active ions was determined by gravimetric analysis (2) or by x-ray absorption techniques (9). The concentrations of Nd^{+3} and Er^{+3} ions were independently determined from oscillator strength measurements. The oscillator strengths of the 580 nm Nd^{+3} absorption band and the 520 nm Er^{+3} absorption band were found to be constant over a large concentration region, thereby allowing the Nd^{+3} or Er^{+3} ion content to be obtained from integrated absorption measurements. The combination of th se two techniques enabled the ion concentration of each species to be determined with an uncerta ty of 5%. Confirming data were also taken using energy dispersive x-ray analysis (EDX).

2) Optical Measurements

The absorption, excitation and emission spectra of the exchanged crystals were recorded on a SPEX F112A spectrofluorimeter. The luminescence lifetime measurements of Ce^{+3} involved excitation of the crystals at 308 nm (Lambda Physik 201 MSC XeCl excimer laser) and detection of the emission (peak at 395nm) with a Hamamatsu S1722-01 Si photodiode. A band pass filter was used to block the signal from the pump beam. The data was collected and averaged by a Tektronix 2430A digital oscilloscope. The temporal response of this system was determined to be 17 nsecs.

Results and Discussion

1) Synthesis

The double ion exchange technique described in the previous section was used with three different lanthanide systems (Ce^{+3}/Nd^{+3}, Ce^{+3}/Tb^{+3}, Er^{+3}/Yb^{+3}) over a wide range of sensitizer-to-activator ratios. The Na^+ ion content of the ß"-alumina crystals was only partially replaced to avoid the concentration quenching effects which have been documented in highly doped materials (10). The resulting crystals can be described by the formula:

$$Na_{1.67-3(xs+xa)}Ln_{xa}Ln_{xs}Mg_{0.67}Al_{10.33}O_{17}$$

where Ln_{xs} and Ln_{xa} denote the lanthanide sensitizer and activator, respectively. The total lanthanide content (x_s+x_a) varied from 0.19 to 0.37 (6 to 12 x 10^{20} ions/cm$^{3)}$ and the sensitizer/activator ratio varied from 0.05 to 4.0. A list of the salt concentrations used and the measured ionic content of the crystals is given in Table 1. In almost all cases, the relative ion concentration of the crystal reflected the relative ion concentration ratio of the molten salts. This behavior is shown in Figure 1 by the good fit of the data points to the straight line which represents the condition where the Ce^{+3}/Nd^{+3} ratio in the melt is equal to that in the crystal after exchange. This linearity over such a wide range of Ce^{+3}/Nd^{+3} values (i.e., from 0.1 to 2.0) indicates that the free energies for the ion exchange of Ce^{+3} and Nd^{+3} from the molten chlorides are comparable. This is not suprising since the thermodynamic properties of the trivalent lanthanides are quite comparable, particularly those with similar atomic number (11). Thus, the Ce^{+3} and Nd^{+3} ions can freely substitute for one another in the crystal without disturbing the equilibrium of the exchange.

The double ion exchange method produces a homogeneous ionic distribution in the crystals. Both optical and ESR spectroscopy studies indicate that the lanthanide ions are uniformly distributed in the crystal with no evidence of ion pairing or aggregation effects. The optical absorption and emission properties of the doubly-doped materials consist of two components: (a) the characteristic spectral properties for each of the lanthanide ions in the ß"-alumina matrix and (b) the sensitizer-to-activator energy transfer. Thus, except for the spectral changes which result from energy transfer, the observed optical properties are those of the free ion in the ß"-alumina matrix. The ESR spectra for the Ce^{+3}/Nd^{+3} samples are consistent with this interpretation since the results represent a superposition of the ESR spectra for the individual Ce^{+3} and Nd^{+3} ions in ß"-alumina (12,13). It is interesting to note that in these Ce^{+3}/Nd^{+3} materials the site occupation of each ion is unaffected by the presence of the other species and both occupy the so-called "mid-oxygen" site of C_{2h} symmetry.

2) Optical Properties

2.1) Energy Transfer in Ce^{+3}/Nd^{+3}-ß"-Alumina

Energy transfer characteristics and processes were studied extensively in the Ce^{+3}/Nd^{+3} samples and, to a lesser extent, in the Ce^{+3}/Tb^{+3} and Yb^{+3}/Er^{+3} samples. The occurrence of energy transfer between Ce^{+3} and Nd^{+3} in the doubly-doped samples is evident from the excitation spectrum of the 890 nm emission band of Nd^{+3} (Figure 2). Unsensitized, Nd^{+3}-ß"-alumina exhibits two excitation peaks in the ultra-violet region of the spectrum. These bands are centered at 345 and 350 nm and correspond to absorption by the ^2L_J, ^2I_J and ^4D_J multiplets. In contrast, the excitation spectrum of the Ce^{+3}/Nd^{+3} crystals has an additional broad excitation band from 220-370 nm which is characteristic of the 4f → 5d transition of Ce^{+3}. This change in the spectrum indicates that interionic energy transfer has occurred since photons absorbed by Ce^{+3} produce
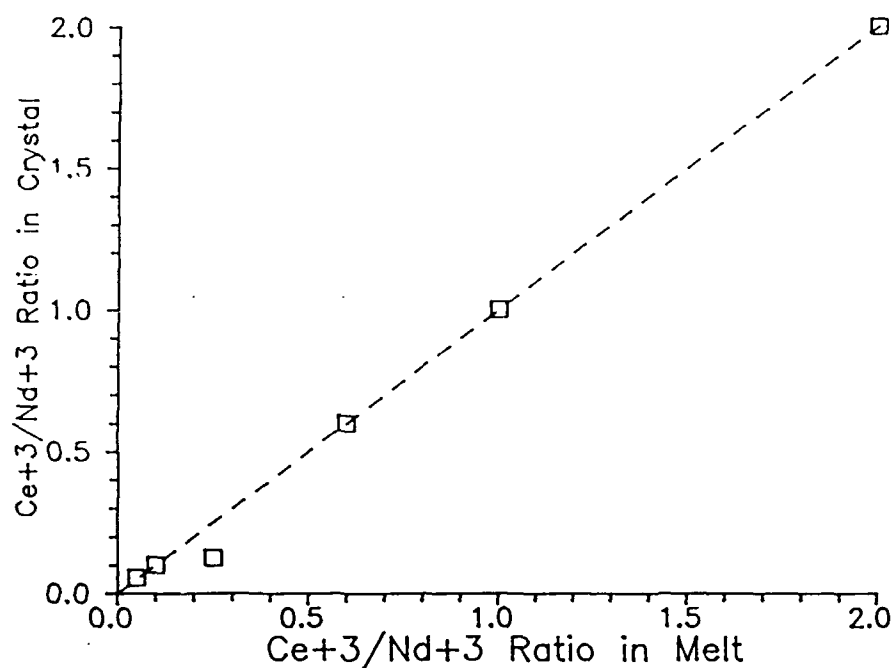
FIG.1

Comparison of the Ce^{+3}/Nd^{+3} ratio in the exchanged ß"-alumina crystal versus that in the melt. The dashed line indicates the condition where the content in the crystal is equal to that in the melt.
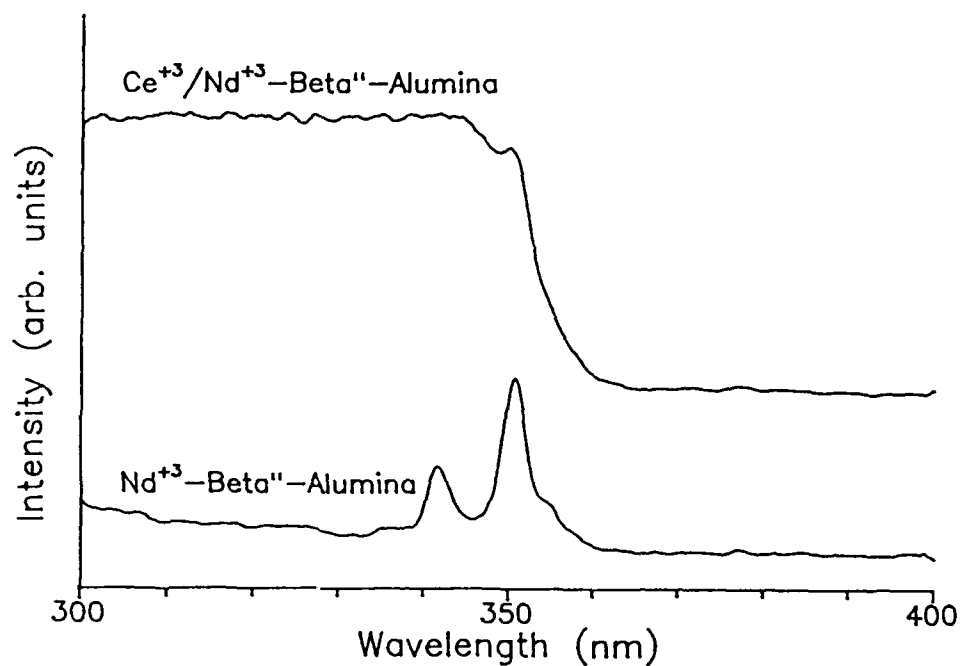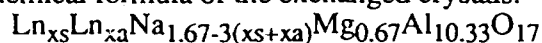

FIG. 2

Excitation spectrum of the 890 nm emission from Ce^{+3}/Nd^{+3}-ß"-alumina $(xs = 0.160; xa = 0.160)$ and from Nd^{+3}-ß"-alumina $(xs = 0; xa = 0.262)$.

TABLE 1:

Energy Transfer Systems Synthesized in ß"-Alumina
By Ion Exchange Techniques

Chemical formula of the exchanged crystals:
$$Ln_{xs}Ln_{xa}Na_{1.67-3(xs+xa)}Mg_{0.67}Al_{10.33}O_{17}$$

x_s = moles of the sensitizer
x_a = moles of the activator

Sens., S	Activ., A	Moles S/Moles A in Molten Salt	Moles S/Moles A in Crystal	x_s	x_a
Ce^{+3}	Nd^{+3}	1/20	1/18	0.016	0.294
		1/10	1/10	0.028	0.282
		1/4	1/8	0.021	0.169
		1/1	1/1	0.160	0.160
		3/5	3/5	0.231	0.139
		2/1	2/1	0.127	0.063
		4/1	10/1	0.336	0.034
Ce^{+3}	Tb^{+3}	1/4	1/5	0.037	0.183
		1/10	1/10	0.017	0.173
Yb^{+3}	Er^{+3}	12/1	10/1	0.279	0.031
		20/1	20/1	0.324	0.016

emission from Nd^{+3}. Some energy transfer in these crystals occurs via radiative processes. The reabsorption of sensitizer photons is evident from the appearance of Nd^{+3} absorption peaks in the Ce^{+3} emission band of the doubly-doped sample.

The use of multiple ion exchange to vary the sensitizer-to-activator ratio was helpful in investigating the energy transfer efficiency in Ce^{+3}/Nd^{+3}-ß"-alumina. The efficiency of nonradiative energy transfer is strongly dependent on the average sensitizer-to-activator distance (7). Since the total lanthanide ion content for all of the ß"-alumina crystals was nearly equal, the sensitizer-to-activator distance is directly proportional to the Ce^{+3}/Nd^{+3} ratio. The nonradiative energy transfer in ß"-alumina was determined by the luminescent decay time measurements of Ce^{+3} both in the absence and presence of the Nd^{+3} activator (τ and τ_0 respectively). The presence of nonradiative transfer shortens the luminescent decay times of the sensitizing ion by providing an alternative pathway for the de-excitation of the excited state energy. From the decay measurements, the nonradiative transfer efficiency, η_T, can be calculated according to the expression (7):

$$\eta_T = 1 - \tau/\tau_0 \tag{1}$$

Figure 3 shows the efficiencies calculated from Equation (1) as a function of the Ce^{+3}/Nd^{+3} ion concentration ratio. The intrinsic decay time of Ce^{+3} in Ce^{+3}-ß"-alumina with a Ce^{+3}

concentration of 0.18×10^{20} ions/cm^3 ($x_s = 0.017$) was determined to be 40 nsecs. The Ce^{+3} decay time shortened with increasing additions of Nd^{+3} indicating an increase in transfer efficiency. This trend is consistent with what is expected for electronic multipolar processes. That is, as the Ce^{+3}/Nd^{+3} ion ratio decreases, the interaction distance between the two ions is reduced and the probability of nonradiative energy transfer beween the ions is increased. Thus, the highest values for the transfer efficiency were measured at the lowest Ce^{+3}/Nd^{+3} ratios. Unfortunately, the transfer efficiency for the crystal containing the lowest Ce^{+3}/Nd^{+3} ratio could not be determined due to the limitations of the temporal response of our equipment. An efficiency in the range of 40% was obtained for ß"-alumina crystals containing one Ce^{+3} for every ten Nd^{+3} ions. The efficiency is even higher for the crystal with greater Nd^{+3} content (Ce^{+3}/Nd^{+3} = 1/20) but the lifetime, τ, was too short to be accurately measured for this sample.
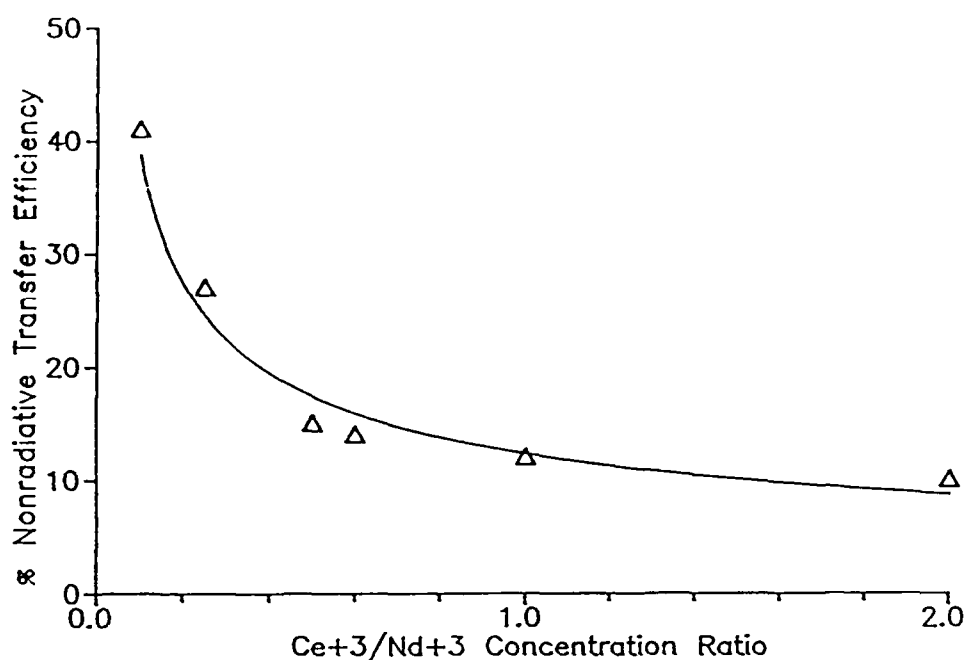
FIG. 3
Energy transfer efficiency as a function of Ce^{+3}/Nd^{+3} concentration ratio for Ce^{+3}/Nd^{+3}-ß"-alumina.

2.2) Energy Transfer in Ce^{+3}/Tb^{+3}-ß"-Alumina

Evidence of energy transfer in Ce^{+3}/Tb^{+3} ß"-alumina samples has also been observed. This couple is often used in phosphor systems as it utilizes the 540 nm emission peak of Tb^{+3} (7). In ß"-alumina, a significant portion of the Ce^{+3} excitation band overlaps with the weaker 4f-4f excitation bands of Tb^{+3} thus greatly increasing the strength and spectral range of absorption. As a result, a six fold increase in the luminescent intensity of the 540 nm emission peak of Tb^{+3} was observed when a crystal containing one Ce^{+3} ion for every ten Tb^{+3} ions was broadband pumped in the near ultraviolet region.

2.3) Up-conversion in Yb^{+3}/Er^{+3}-ß"-Alumina

The Yb^{+3}/Er^{+3} couple is well known for its ability to produce up-conversion. This process involves the stepwise excitation of the Er^{+3} ion by the addition of nonradiative energy transferred from Yb^{+3} (14). To insure a high transfer rate, the double-doped ß"-alumina crystals were prepared containing a high Yb^{+3} content. The occurrence of up-conversion processes in ß"-alumina was investigated by exciting each crystal at 970 nm, the maximum absorption wavelength of Yb^{+3} in the ß"-alumina host. In each Yb^{+3}/Er^{+3}-ß"-alumina crystal synthesized, infrared-to-visible up-conversion was achieved and both green (525 nm peak) and red (645 nm peak) emission bands were observed. Neither emission band was detected when crystals doped only with Er^{+3} or only with Yb^{+3} were excited at 970 nm. The shape and position of each band coincides with those measured from Er^{+3}-ß"-alumina crystals excited with 376 nm luminescence verifying the existence of up-conversion processes.

Conclusions

The unique ion exchange chemistry of the ß"-aluminas enables two different lanthanide species to be simultaneously introduced into the ß"-alumina structure. This multiple ion exchange process is aided by the fact that the thermodynamic equilibrium established in the eutectic melts is relatively unaffected by the types of trivalent lanthanide ions present. Thus, the different lanthanide ions can freely substitute for one another and the lanthanide concentration in the crystal (after ion exchange) is essentially controlled by the chemistry of the molten salt bath. The double-doping process was used to produce ß"-alumina crystals containing a wide range of sensitizer/activator ratios. The ions were homogeneously distributed in the crystal and energy transfer effects, including up-conversion processes, were demonstrated. The double ion exchange approach is particularly important for exploring novel energy transfer schemes using lanthanides because the process circumvents problems such as ion pairing and segregation which frequently plague the traditional, melt grown, optical materials.

Acknowledgements

References

1. G.C. Farrington and B. Dunn, Solid State Ionics, 7, 267 (1982).

2. B. Dunn and G.C. Farrington, Solid State Ionics, 9&10, 223 (1983).

3. M. Jansen, A.J. Alfrey, O.M. Stafsudd, D.L. Yang, B. Dunn and G. Farrington, Optics Letters, 9, 119 (1984).

4. J.D. Barrie, B. Dunn, O.M. Stafsudd and P. Nelson, J. Lumin., 37, 303 (1987).

5. M.A. Saltzberg, P.K. Davies and G.C. Farrington, Mat. Res. Bull., 21, 1533 (1986).

6. R.C. Powell , G. Venikouas, L. Xi and J.B. Bates, J. Lumin., 37, 1 (1987).

7. R. Reisfeld and C.K. Jorgensen, Lasers and Excited States of Rare Earths, Springer-Verlag, Berlin (1977).

8. M.D. Taylor, J. Inorg. Nucl. Chem., 24, 387 (1962).

9. J. Tegenfeldt, M. Underwood and G.C. Farrington, Solid State Ionics, 18&19, 668 (1986).

10. H.G. Danielmeyer, J. Lumin., 12/13, 179 (1976).

11. D. Brown, Halides of the Lanthanides and Actinides, Wiley-Interscience, London (1968).

12. J.D. Barrie, L.A. Momoda, B. Dunn, D. Gourier, G. Aka and D. Vivien, submitted for publication.

13. B. Dunn, D.L. Yang and D. Vivien, J. Solid State Chem., 73, 235 (1988).

14. F. Auzel, Proc. IEEE, 6, 758 (1973).